

PHOSPHITE ESTER ADDITIVE COMPOSITIONS

This application claims priority from United States provisional patent application serial number 60/273,303 filed March 2, 2001, United States provisional patent application serial number 60/314,181 filed August 16, 2001, and United States provisional patent application serial number 60/315,746 filed August 29, 2001.

Technical Field

The invention relates generally to improving the performance and reducing the heavy metal content of PVC compounds by the partial or total substitution of conventional mixed metal stabilizers with phosphite esters, or blends thereof, with an effective amount of added zinc.

Background of the Invention

The PVC industry began with the invention of plasticized polyvinyl chloride ("PVC") by Waldo Semon of the B. F. Goodrich Company in 1933 as an alternative to natural rubber where its non-flammability made it ideal for wire insulation, particularly on naval ships. However, unlike rubber, PVC has a tendency to discolor and is not easy to process well. Stabilization is required to perform two basic functions: (1) prevent discoloration; and (2) absorb hydrogen chloride (HCl) which evolves during process. It is believed that billions of pounds of flexible PVC are employed throughout the world in a wide variety of commercial applications. These include vinyl flooring, wall covering, roofing, pond and pool liners, film, upholstery, apparel, hose, tubing and wire insulation.

In order to successfully process vinyl compounds into finished vinyl articles by extrusion, calendaring or molding, it is necessary to incorporate between one and five percent of a heat stabilizer to prevent dehydrohalogenation and discoloration of the polymer during thermal processing. The preferred vinyl heat stabilizers for most flexible PVC applications in the United States are referred to as "Mixed Metal" heat stabilizers. They are complex multi-component chemical admixtures based upon combinations of alkaline earth and heavy metal salts with a variety of antioxidants, HCl absorbers and chelating agents. The most widely used mixed metals are based upon and referred to as Barium-Cadmium, Barium-Cadmium-Zinc, Barium-Zinc and Calcium-Zinc stabilizers. However, mixed metal heat stabilizers suffer from several drawbacks. If the level of zinc is too high, the polymer will char very rapidly. Additionally, barium and cadmium are toxic heavy metals which while they do provide heat stability, their presence adversely affects

1 clarity, plate out and stain. In order to counteract these negative effects, further additional
2 components were blended into the formulations, making PVC additive formulation and
3 processing a highly unique and specialized art. Clearly, what was needed was an
4 approach which used higher performance phosphites and added back only what was
5 needed.

1 These and other objects of the present invention will become more readily apparent
2 from a reading of the following detailed description taken in conjunction with the
3 accompanying drawings wherein like reference numerals indicate the parts and appended
4 claims.

5 ***Brief Description of the Drawings***

6 The invention may take physical form in certain parts and arrangements of parts, a
7 preferred embodiment of which will be described in detail in the specification and illustrated
8 in the accompanying drawings which form a part hereof, and wherein:

9 FIG. 1 is a graph over time of the impact on oven aging by varying the class of
10 phosphite stabilizer used to stabilize PVC (as measured by Yellowness Index) using 100
11 parts PVC resin, 45 parts dioctyl phthalate, 20 parts CaCO_3 , 5 parts epoxidized soybean
12 oil, 0.25 parts stearic acid, 0.2 parts zinc stearate, and 2 parts of various classes of
13 phosphites;

14 FIG. 2 is a graph over time of the impact of oven aging by varying the amount of
15 added zinc used with diphenyl ethylhexyl phosphite (as measured by Yellowness Index)
16 using 100 parts PVC resin, 45 parts dioctyl phthalate, 20 parts CaCO_3 , 5 parts epoxidized
17 soybean oil, 0.25 parts stearic acid, 2 parts diphenyl ethylhexyl phosphite, and various
18 amounts of zinc stearate;

19 FIG. 3 is a graph over time of the impact on oven aging by varying the amount of
20 tetraisodecyl bisphenol A diphosphite used to stabilize PVC (as measured by Yellowness
21 Index) using 100 parts PVC resin, 45 parts dioctyl phthalate, 20 parts CaCO_3 , 5 parts
22 epoxidized soybean oil, and 0.2 parts zinc stearic acid and various amounts of bisphenol A-
23 based phosphite;

24 FIG. 4 is a graph over time of the impact on oven aging by varying the phosphite or
25 phosphite blend used to stabilize PVC (as measured by Yellowness Index) using 100 parts
26 PVC resin, 45 parts dioctyl phthalate, 20 parts CaCO_3 , 5 parts epoxidized soybean oil, and
27 0.25 parts stearic acid, 0.25 parts zinc stearate and 2.0 parts phosphite or phosphite blend;

28 FIG. 5 is a graph over time of the impact on oven aging by comparing a phosphite of
29 the instant invention (i.e., tetraisodecyl bisphenol-A diphosphite / poly DPG phenyl
30 phosphite blend with 2.5% zinc octanoate) to Prior Art PVC stabilizers (as measured by
31 Yellowness Index) using 100 parts PVC resin, 25 parts dioctyl phthalate, 25 parts CaCO_3 ,
32 3 parts epoxidized soybean oil, 7.0 parts TiO_2 , and 0.5 parts stearic acid and 4 parts of
33 stabilizer;

FIG. 6 is a graph over time of the impact on the QUV weathering test by comparing a phosphite of the instant invention (i.e., tetraisodecyl bisphenol-A diphosphite / poly DPG phenyl phosphite blend containing 2.5% zinc octanoate) to Prior Art PVC stabilizers (as measured by Yellowness Index) using 100 parts PVC resin, 55 parts 7-11, 3 parts epoxidized soybean oil, 7.0 parts TiO₂, and 0.3 parts stearic acid and 3.5 parts of stabilizer; and

FIG. 7 is a bar chart of percentage weight loss of various stabilizers and a phosphite ester blend of the present invention after 2 hours at 110°C illustrated in Table VI.

Detailed Description of the Invention

Referring now to the drawings wherein the showings are for purposes of illustrating the preferred embodiment of the invention only and not for purposes of limiting the same, the Figures show various comparisons of phosphite ester / Zn additive compositions with that of various Prior Art additives. As illustrated in FIG. 1, the efficacy of all classes of phosphites is not equivalent. The hydrogen phosphites are the least effective class of phosphite esters, whereas the bisphenol-A phosphites as well as the dipropylene glycol phosphites showed extended resistance to yellowing over time. Within each class of phosphite, the performance for particular phosphites was very similar.

The level of zinc present in the stabilizer affects the performance of the additive. As noted in the Prior Art, early color is improved with added zinc. However, as shown in FIG. 2, a window of optimum zinc level exists, the specific range of the window being somewhat unique for each phosphite class. If the zinc concentration is too low, the early color will not be acceptable. If the zinc concentration is too high, the PVC will char at earlier exposure times. This effect is displayed for an alkyl-aryl phosphite (i.e., diphenyl ethylhexyl phosphite) in FIG. 2, although the relationship is demonstrated for all classes of phosphite esters.

Although the zinc level has an optimum value for effectiveness, the level of phosphite does not appear to be as sensitive. In general, the long-term color improved with an increase in the level of phosphite as shown in FIG. 3. The increase in phosphite level (i.e., Doverphos[®] 675, a C₁₀ bisphenol A phosphite) had little effect on the color of the PVC strip before 50 minutes, but extended the final char time to greater than 120 minutes. Again, this trend was observed for most classes of phosphites. Thus phosphites can replace other heavy metal stabilizers by complexing acidic Zn, in addition to reacting with labile chlorides and HCl.

1 Synergistic effects were observed using combinations of phosphite classes. FIG. 4
2 displays blends of alkyl-aryl, DPG and BPA based phosphites. The total concentration of
3 phosphite remained constant at 2.0 parts. It is obvious that the addition of a higher